Brazilian Journal<br>of Chemical<br>Engineering

ISSN 0104-6632

# LIQUID-LIQUID EQUILIBRIA OF PROPIONIC ACID - WATER - SOLVENT (n-HEXANE, CYCLOHEXANE, CYCLOHEXANOL AND CYCLOHEXYL ACETATE) TERNARIES AT 298.15 K 

D. Özmen, U. Dramur and B. Tatli<br>Department of Chemical Engineering, Istanbul University, 34850, Avcilar - Istanbul, Turkey<br>E-mail: dilekus@istanbul.edu.tr

(Received: May 21, 2003 ; Accepted: May 28, 2004)


#### Abstract

The experimental liquid-liquid equilibrium data on propionic acid-water-solvent ternary mixtures at a temperature of 298.15 K are presented. The solvents are n -hexane, cyclohexane, cyclohexanol and cyclohexyl acetate. The distribution coefficients and separation factors are reported. The tie line data are correlated using the methods of Othmer-Tobias and Hand. The experimental results are compared with the values predicted by the UNIFAC group-contribution method. Keywords: liquid-liquid equilibria, propionic acid, UNIFAC.


## INTRODUCTION

Liquid-liquid equilibria are of interest in extraction operations and are useful for developing a thermodynamic predictive and correlative method. Liquid extraction of propionic acid from aqueous solutions with various solvents has been reviewed by several researchers (Badakhshan et al., 1985; Arce et al., 1993, 1995; Yoshizawa et al., 1994; Sólimo et al., 1997; Radwan et al., 1997; Zurita et al., 1998; Cehreli et al., 1999). To be able to choose the most suitable agent for extraction of propionic acid from aqueous solutions, experimental liquidliquid equilibrium data were determined for propionic acid - water - solvent ternary mixtures at a temperature of 298.15 K .

The solvents used are n-hexane, cyclohexane, cyclohexanol and cyclohexyl acetate. The distribution coefficients and separation factors were obtained from experimental results and are also reported. The tie lines were determined and were
correlated by the methods of Othmer-Tobias and Hand on a mass-fraction basis. The experimental results are compared with values predicted by the UNIFAC group-contribution method, using a calculating program in MATLAB.

## EXPERIMENTAL

## Materials

Propionic acid was furnished by Fluka. Other chemicals were used as received from Merck. The purity of the chemicals was checked on the basis of their refractive indexes at $293.15 \pm 0.20 \mathrm{~K}$. Refractive indexes were measured with an AbbéHilger refractometer with a stated accuracy of $\pm 0.0001 \mathrm{n}_{\mathrm{D}}$. The measured physical properties are listed in Table 1 along with values from the literature (Weast, 1990). Deionized water was further distilled before use.

Table 1: Physical Properties of the Chemicals.

| Chemical | $\mathbf{M}[\mathbf{g} / \mathbf{g}-\mathbf{m o l}]^{*}$ | $\mathbf{d}[\mathbf{k g} /]^{*}$ | b.p. $\left[^{\circ} \mathbf{C}\right]^{*}$ | Refractive Index $\left(\mathbf{2 0}{ }^{\circ} \mathbf{C}\right)$ |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | Exp. |  |
| Propionic acid | 74.08 | 0.9930 | 141.00 | 1.3809 | 1.3863 |
| n-Hexane | 86.18 | 0.6603 | 69.00 | 1.3751 | 1.3753 |
| Cyclohexane | 84.16 | 0.7785 | 80.70 | 1.4266 | 1.4275 |
| Cyclohexanol | 100.16 | 0.9624 | 161.10 | 1.4641 | 1.4657 |
| Cyclohexyl Acetate | 142.20 | 0.9698 | 173.62 | 1.4401 | 1.4406 |

* Weast. R.C., Handbook of Chemistry and Physics, CRC Press, Boca Raton, Florida (1989-1990).


## Procedure

Data for the solubility curve of the ternary systems were determined by the cloud point method (Alders, 1959; Cehreli, 2002). Solubility curve data determinations were made in an equilibrium cell equipped with a magnetic stirrer and an isothermal fluid jacket. The temperature of the mixture was controlled by a bath within an accuracy of $\pm 0.2 \mathrm{~K}$. The inner temperature of the cell was measured within an accuracy of $\pm 0.1 \mathrm{~K}$ by a certified Fischer thermometer.

The cell, designed to contain a solution of 50$200 \mathrm{~cm}^{3}$, was filled with homogeneous waterpropionic acid mixtures prepared by weighing. An electronic Sauter balance with an accuracy of $\pm 0.1$ mg was used. The solvent was added by means of an automatic microburet with an accuracy of $\pm 0.005$ $\mathrm{cm}^{3}$. The end point was determined by observing the transition from $a$ homogeneous to $a$ heterogeneous mixture. This pattern was convenient for providing the water-rich side of the curves. On the other hand, data for the solvent-rich side of the curves were it became obtained by titrating homogeneous propionic acid-solvent with water until a turbid. Composition determinations were accurate to $\pm 0.0005$ mass fraction.

The solubilities of water and solvent were determined by applying a synthetic method. A weighed amount of the first substance was introduced into the cell; the second was added until
permanent heterogeneity had been observed. An ultra-accurate titrator with an accuracy of $\pm 0.001$ $\mathrm{cm}^{3}$ was used.

The tie line data determinations were obtained using the equilibrium apparatus described above. A variety of mixtures within the heterogeneous gap were prepared for the four systems studied. The cell was filled with each of these mixtures and vigorously stirred for 1 h under isothermal conditions. After the stirrer was turned off, the contents were immediately introduced into the vertical settler, also equipped with an isothermal jacket. After complete separation of the phases, a suitable amount of each layer was removed for analysis. The acid contents of the samples were determined by volumetric titration with 0.1 N NaOH solution by using ethanolic phenolphthalein. Several check determinations on known samples showed the accuracy of the method was within $\pm 0.001$ of the mass fraction.

## RESULTS AND DISCUSSION

The measured values for solubility curves and experimental mutual solubilities for the propionic acid - water - n-hexane, propionic acid - water cyclohexane, propionic acid - water - cyclohexanol and propionic acid - water - cyclohexyl acetate systems are reported in Tables 2-5. The tie line compositions for the these systems are given in Table 6.

Table 2:The Solubility Curve Data for the Propionic Acid
(1)-Water (2)-n-Hexane (3) System at 298.15 K.

| Exp. No. | $\mathbf{W}_{\mathbf{1}}$ | $\mathbf{W}_{\mathbf{2}}$ | $\mathbf{W}_{\mathbf{3}}$ |
| :---: | :---: | :---: | :---: |
| 1 | 0.00 | 1.38 | 98.62 |
| 2 | 9.96 | 1.38 | 88.66 |
| 3 | 20.57 | 1.29 | 78.14 |
| 4 | 31.07 | 1.15 | 67.78 |
| 5 | 39.74 | 1.85 | 58.41 |
| 6 | 57.85 | 3.60 | 38.55 |
| 7 | 58.47 | 3.59 | 37.94 |
| 8 | 66.42 | 5.18 | 28.40 |
| 9 | 73.57 | 7.89 | 18.54 |
| 10 | 71.95 | 9.92 | 18.13 |
| 11 | 76.20 | 15.37 | 8.43 |
| 12 | 68.24 | 30.40 | 1.36 |
| 13 | 68.37 | 30.45 | 1.18 |
| 14 | 59.13 | 40.46 | 0.41 |
| 15 | 49.75 | 50.08 | 0.17 |
| 16 | 39.87 | 59.94 | 0.19 |
| 17 | 29.97 | 69.84 | 0.19 |
| 18 | 20.26 | 79.47 | 0.27 |
| 19 | 10.25 | 89.46 | 0.29 |
| 20 | 0.00 | 99.05 | 0.95 |

Table 3: The Solubility Curve Data for the Propionic Acid (1)-Water (2)-Cyclohexane (3) System at 298.15 K.

| Exp. No. | $\mathbf{W}_{\mathbf{1}}$ | $\mathbf{W}_{\mathbf{2}}$ | $\mathbf{W}_{\mathbf{3}}$ |
| :---: | :---: | :---: | :---: |
| 1 | 0.00 | 99.90 | 0.10 |
| 2 | 10.66 | 89.08 | 0.26 |
| 3 | 20.11 | 79.70 | 0.19 |
| 4 | 29.26 | 70.57 | 0.17 |
| 5 | 44.17 | 55.39 | 0.44 |
| 6 | 58.65 | 40.52 | 0.83 |
| 7 | 70.60 | 13.07 | 16.33 |
| 8 | 71.17 | 26.88 | 1.95 |
| 9 | 64.61 | 8.48 | 26.91 |
| 10 | 60.49 | 6.05 | 33.46 |
| 11 | 59.99 | 4.33 | 37.68 |
| 12 | 44.42 | 1.46 | 54.12 |
| 13 | 32.69 | 0.31 | 67.00 |
| 14 | 15.49 | 0.25 | 84.26 |
| 15 | 0.00 | 0.42 | 99.58 |

Table 4: The Solubility Curve Data for the Propionic Acid (1)-Water (2)-Cyclohexanol (3) System at 298.15 K.

| Exp. No. | $\mathbf{W}_{\mathbf{1}}$ | $\mathbf{W}_{\mathbf{2}}$ | $\mathbf{W}_{\mathbf{3}}$ |
| :---: | ---: | ---: | ---: |
| 1 | 0.00 | 97.84 | 2.16 |
| 2 | 17.09 | 78.39 | 4.52 |
| 3 | 18.90 | 75.84 | 5.26 |
| 4 | 21.00 | 71.07 | 7.93 |
| 5 | 26.59 | 58.71 | 14.70 |
| 6 | 29.75 | 49.16 | 21.09 |
| 7 | 32.83 | 40.11 | 27.06 |
| 8 | 32.38 | 34.23 | 33.39 |
| 9 | 32.54 | 26.95 | 40.51 |
| 10 | 29.00 | 21.80 | 49.20 |
| 11 | 21.65 | 15.78 | 62.57 |
| 12 | 12.85 | 8.91 | 78.24 |
| 13 | 0.00 | 8.00 | 92.00 |

Table 5: The Solubility Curve Data for the Propionic Acid (1)-Water (2)-Cyclohexyl Acetate (3) System at 298.15 K.

| Exp. No. | $\mathbf{W}_{\mathbf{1}}$ | $\mathbf{W}_{\mathbf{2}}$ | $\mathbf{W}_{\mathbf{3}}$ |
| :---: | ---: | ---: | ---: |
| 1 | 0.00 | 0.56 | 99.44 |
| 2 | 10.14 | 0.52 | 89.34 |
| 3 | 19.77 | 2.60 | 77.63 |
| 4 | 28.56 | 5.34 | 66.10 |
| 5 | 35.79 | 8.99 | 55.22 |
| 6 | 42.77 | 13.53 | 43.70 |
| 7 | 46.34 | 20.44 | 33.22 |
| 8 | 46.00 | 34.00 | 20.00 |
| 9 | 43.50 | 44.84 | 11.66 |
| 10 | 37.45 | 55.87 | 6.68 |
| 11 | 30.02 | 69.47 | 0.51 |
| 12 | 24.80 | 74.52 | 0.68 |
| 13 | 19.52 | 79.98 | 0.50 |
| 14 | 15.55 | 84.41 | 0.04 |
| 15 | 10.32 | 89.60 | 0.08 |
| 16 | 0.00 | 99.95 | 0.05 |

Brazilian Journal of Chemical Engineering

Table 6: The Tie Line Compositions for the Propionic Acid-Water-Solvent System at 298.15 K.

| Exp. <br> No. | Overall |  |  | Water-rich phase |  |  | Solvent-rich phase |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{W}_{1}$ | $\mathrm{W}_{2}$ | $\mathrm{W}_{3}$ | $\mathrm{W}_{12}$ | $\mathrm{W}_{22}$ | $\mathrm{W}_{32}$ | $\mathrm{W}_{13}$ | $\mathrm{W}_{23}$ | $\mathbf{W}_{33}$ |
| Propionic Acid (1)-Water (2)-n-Hexane (3) System |  |  |  |  |  |  |  |  |  |
| 1 | 4.97 | 55.09 | 39.94 | 6.74 | 92.95 | 0.31 | 1.32 | 1.41 | 97.27 |
| 2 | 10.33 | 50.41 | 39.26 | 13.78 | 86.08 | 0.14 | 4.17 | 1.38 | 94.45 |
| 3 | 15.20 | 45.07 | 39.73 | 19.58 | 80.19 | 0.23 | 8.12 | 1.32 | 90.56 |
| 4 | 20.15 | 40.21 | 39.64 | 26.32 | 73.33 | 0.35 | 12.55 | 1.25 | 86.20 |
| 5 | 25.35 | 35.00 | 39.65 | 34.04 | 65.62 | 0.34 | 16.42 | 1.22 | 82.36 |
| 6 | 30.05 | 30.38 | 39.57 | 39.01 | 60.73 | 0.26 | 21.35 | 1.22 | 77.43 |
| 7 | 39.81 | 30.43 | 29.76 | 49.22 | 50.71 | 0.07 | 22.56 | 1.08 | 76.36 |
| 8 | 49.42 | 26.52 | 24.06 | 57.86 | 41.98 | 0.16 | 27.77 | 1.32 | 70.91 |
| 9 | 59.87 | 20.27 | 19.86 | 66.80 | 32.14 | 1.06 | 38.16 | 1.71 | 60.13 |
| 10 | 69.67 | 15.12 | 15.21 | 73.83 | 22.37 | 3.80 | 51.35 | 2.66 | 45.99 |
| Propionic Acid (1)-Water (2)-Cyclohexane (3) System |  |  |  |  |  |  |  |  |  |
| 1 | 10.11 | 45.35 | 44.54 | 15.64 | 84.16 | 0.20 | 3.66 | 0.52 | 95.82 |
| 2 | 19.98 | 40.09 | 39.93 | 28.87 | 70.80 | 0.33 | 10.13 | 0.41 | 89.46 |
| 3 | 30.09 | 34.96 | 34.95 | 42.00 | 57.74 | 0.26 | 16.36 | 0.22 | 83.42 |
| 4 | 36.36 | 36.14 | 27.50 | 46.90 | 52.78 | 0.32 | 17.96 | 0.18 | 81.86 |
| 5 | 49.81 | 25.15 | 25.04 | 64.60 | 32.62 | 2.78 | 27.51 | 0.12 | 72.37 |
| 6 | 59.88 | 19.92 | 20.20 | 70.17 | 22.63 | 7.20 | 36.92 | 0.57 | 62.51 |
| Propionic Acid (1)-Water (2)-Cyclohexanol (3) System |  |  |  |  |  |  |  |  |  |
| 1 | 5.25 | 57.66 | 37.09 | 2.83 | 95.09 | 2.08 | 8.76 | 9.14 | 82.10 |
| 2 | 10.35 | 52.25 | 37.40 | 5.85 | 91.90 | 2.25 | 15.39 | 11.03 | 73.58 |
| 3 | 16.10 | 47.96 | 35.94 | 9.01 | 88.35 | 2.64 | 22.34 | 14.35 | 63.31 |
| 4 | 20.77 | 41.90 | 37.33 | 11.13 | 85.84 | 3.03 | 26.44 | 17.68 | 55.88 |
| 5 | 25.98 | 35.93 | 38.09 | 13.66 | 82.65 | 3.69 | 30.24 | 23.36 | 46.40 |
| Propionic Acid (1)-Water (2)-Cyclohexyl Acetate (3) System |  |  |  |  |  |  |  |  |  |
| 1 | 5.11 | 54.72 | 40.17 | 4.55 | 95.29 | 0.16 | 6.69 | 0.25 | 93.06 |
| 2 | 10.19 | 49.99 | 39.82 | 7.75 | 92.13 | 0.12 | 11.71 | 0.67 | 87.62 |
| 3 | 14.94 | 45.83 | 39.23 | 11.35 | 88.59 | 0.06 | 18.24 | 2.11 | 79.65 |
| 4 | 19.88 | 41.05 | 39.07 | 14.55 | 85.41 | 0.04 | 24.73 | 4.20 | 71.07 |
| 5 | 24.92 | 36.00 | 39.08 | 17.42 | 82.51 | 0.07 | 30.76 | 6.45 | 62.79 |
| 6 | 29.82 | 31.03 | 39.15 | 20.84 | 78.95 | 0.21 | 35.10 | 8.36 | 56.54 |
| 7 | 35.00 | 25.38 | 39.62 | 24.10 | 75.42 | 0.48 | 39.40 | 10.82 | 49.78 |
| 8 | 40.01 | 20.31 | 39.68 | 27.56 | 71.44 | 1.00 | 43.79 | 14.87 | 41.34 |
| 9 | 38.43 | 46.66 | 14.91 | 34.68 | 61.98 | 3.34 | 46.92 | 23.84 | 29.24 |

## Distribution Coefficients and Separation Factors

$$
\begin{equation*}
\mathrm{D}_{\mathrm{i}}=\mathrm{W}_{\mathrm{i} 3} / \mathrm{W}_{\mathrm{i} 2} \tag{1}
\end{equation*}
$$

Distribution coefficients, $D_{i}$, for propionic acid ( $\mathrm{i}=1$ ) and water $(\mathrm{i}=2)$ and separation factors, S, were determined (where $3=$ solvent) as follows:

$$
\begin{equation*}
\mathrm{S}=\mathrm{D}_{1} / \mathrm{D}_{2} \tag{2}
\end{equation*}
$$

Results are listed in Table 7.

Table 7: Experimental Distribution Coefficients $\left(D_{i}\right)$ of the Propionic Acid and Water and Separation Factors (S) at 298.15 K.
a) Propionic Acid (1)-Water (2)-n-Hexane
(3) System

| Exp. <br> No. | $\mathbf{D}_{\mathbf{1}}$ | $\mathbf{D}_{\mathbf{2}}$ | $\mathbf{S}$ |
| :---: | :---: | :---: | :---: |
|  | $\mathbf{W}_{\mathbf{2 3}} / \mathbf{W}_{\mathbf{2 2}}$ | $\mathbf{D}_{\mathbf{1}} / \mathbf{D}_{\mathbf{2}}$ |  |
| 1 | 0.20 | 0.02 | 12.87 |
| 2 | 0.30 | 0.02 | 18.89 |
| 3 | 0.41 | 0.02 | 25.26 |
| 4 | 0.48 | 0.02 | 27.91 |
| 5 | 0.48 | 0.02 | 25.94 |
| 6 | 0.55 | 0.02 | 27.17 |
| 7 | 0.46 | 0.02 | 21.51 |
| 8 | 0.48 | 0.03 | 15.27 |
| 9 | 0.57 | 0.05 | 10.74 |
| 10 | 0.70 | 0.12 | 5.85 |

b) Propionic Acid (1)-Water (2)Cyclohexanol (3) System

| Exp. No. | $\mathbf{D}_{\mathbf{1}}$ | $\mathbf{D}_{\mathbf{2}}$ | $\mathbf{S}$ |
| :---: | :---: | :---: | :---: |
|  | $\mathbf{W}_{\mathbf{1 3}} / \mathbf{W}_{\mathbf{1 2}}$ | $\mathbf{W}_{\mathbf{2 3}} / \mathbf{W}_{\mathbf{2 2}}$ | $\mathbf{D}_{\mathbf{1}} / \mathbf{D}_{\mathbf{2}}$ |
| 1 | 3.10 | 0.10 | 32.20 |
| 2 | 2.63 | 0.12 | 21.92 |
| 3 | 2.48 | 0.16 | 15.27 |
| 4 | 2.38 | 0.21 | 11.53 |
| 5 | 2.21 | 0.28 | 7.83 |
| - | - | - | - |

## Correlations

The reliability of experimentally measured tie line data is ascertained by applying the OthmerTobias (Eq. 3) and Hand (Eq. 4) equations (Othmer and Tobias, 1942; Brandani and Ross, 1985).
$\ln \frac{\left[\left(1-\mathrm{W}_{33}\right)\right]}{\mathrm{W}_{33}}=\mathrm{a}_{1}+\mathrm{b}_{1} \ln \frac{\left[\left(1-\mathrm{W}_{22}\right)\right]}{\mathrm{W}_{22}}$
c) Propionic Acid (1)-Water (2)-Cyclohexyl Acetate (3) System

| Exp. $\mathbf{N o}$ | $\mathbf{D}_{\mathbf{1}}$ | $\mathbf{D}_{\mathbf{2}}$ | $\mathbf{S}$ |
| :---: | :---: | :---: | :---: |
|  | $\mathbf{W}_{\mathbf{1 3}} / \mathbf{W}_{\mathbf{1 2}}$ | $\mathbf{W}_{\mathbf{2 3}} / \mathbf{W}_{\mathbf{2 2}}$ | $\mathbf{D}_{\mathbf{1}} / \mathbf{D}_{\mathbf{2}}$ |
| 1 | 1.47 | 0.00 | 558.21 |
| 2 | 1.51 | 0.01 | 208.52 |
| 3 | 1.61 | 0.02 | 67.41 |
| 4 | 1.70 | 0.05 | 34.56 |
| 5 | 1.77 | 0.08 | 22.58 |
| 6 | 1.68 | 0.11 | 15.90 |
| 7 | 1.63 | 0.14 | 11.39 |
| 8 | 1.59 | 0.21 | 7.63 |
| 9 | 1.35 | 0.38 | 3.52 |
| - | - | - | - |

d) Propionic Acid (1)-Water (2)Cyclohexane (3) System

| Exp. No. | $\mathbf{D}_{\mathbf{1}}$ | $\mathbf{D}_{\mathbf{2}}$ | $\mathbf{S}$ |
| :---: | :---: | :---: | :---: |
|  | $\mathbf{W}_{\mathbf{1 3}} / \mathbf{W}_{\mathbf{1 2}}$ | $\mathbf{W}_{\mathbf{2 3}} / \mathbf{W}_{\mathbf{2 2}}$ | $\mathbf{D}_{\mathbf{1}} / \mathbf{D}_{\mathbf{2}}$ |
| 1 | 0.23 | 0.00 | 98.52 |
| 2 | 0.35 | 0.00 | 75.17 |
| 3 | 0.39 | 0.00 | 87.52 |
| 4 | 0.38 | 0.01 | 64.13 |
| 5 | 0.43 | 0.09 | 5.00 |
| 6 | 0.53 | 0.32 | 1.65 |

$$
\begin{equation*}
\ln \left(\mathrm{W}_{13} / \mathrm{W}_{33}\right)=\mathrm{a}_{2}+\mathrm{b}_{2} \ln \left(\mathrm{~W}_{12} / \mathrm{W}_{22}\right) \tag{4}
\end{equation*}
$$

The correlations are shown in Figures 1 and 2. The correlation coefficients and correlation factor $\left(\mathrm{r}^{2}\right)$ values were determined by the least-squares method and are given in Table 8.

The liquid-liquid equilibria of the ternary mixtures were also predicted using the UNIFAC
method (Fredenslund et al., 1975). For this purpose, the MATLAB program is used. The groupinteraction parameters used for estimating the activity coefficients in the liquid phases were those obtained from experimental equilibrium results. The predicted liquid-liquid equilibria data are plotted in Figures 3-6 along with the experimental values.

Group volumes $\left(\mathrm{R}_{\mathrm{k}}\right)$ and surface areas $\left(\mathrm{Q}_{\mathrm{k}}\right)$ needed by UNIFAC are shown in Table 9. UNIFAC liquid-liquid equilibrium parameters ( $\mathrm{a}_{\mathrm{mn}}$ ) representing interactions between 7 groups are shown in Table 10 (Reid, 1987).

The deviations shown in the figures are presented numerically by applying the root mean square (RMSD). RMSDs are calculated from the


Figure 1: Othmer-Tobias Plot for the PropionicAcid (1)-Water (2)-Solvent (3) System at 298.15 K
difference between the experimental data and the predictions of each system according to the following formula:
$\operatorname{RMSD}=\left\{\sum_{\mathrm{k}}\left[\sum_{\mathrm{j}}\left(\sum_{\mathrm{i}}\binom{\left.\mathrm{W}_{\mathrm{i}, \mathrm{exp}}-\right)^{2}}{-\mathrm{W}_{\mathrm{i}, \mathrm{calc}}}^{2}\right)\right] / 6 \mathrm{n}\right\}^{1 / 2}$
where $W_{i, \exp }$ is the experimental mass fraction of the tie lines; $\mathrm{W}_{\mathrm{i}, \text { calc }}$ is the calculated mass fraction of the tie lines; $\mathrm{k}=1,2,3, \ldots, \mathrm{n}$ (tie lines); j is the waterrich or solvent-rich phase and i is the number of components (Fandary et al., 1999).

The root mean square deviation values for the systems studied are presented in Table 11.


Figure 2: Hand Plot for the Propionic Acid (1)Water (2)-Solvent (3) System at 298.15 K

Table 8: The Correlation Coefficients and Correlation Factors
for the Othmer-Tobias and Hand Correlations.

|  | Othmer-Tobias coefficients |  |  | Hand coefficients |  |  |
| :--- | ---: | ---: | :---: | :---: | :---: | :---: |
| Systems | $\mathbf{a}_{\mathbf{1}}$ | $\mathbf{b}_{\mathbf{1}}$ | $\mathbf{r}^{\mathbf{2}}$ | $\mathbf{a}_{\mathbf{2}}$ | $\mathbf{b}_{\mathbf{2}}$ | $\mathbf{r}^{\mathbf{2}}$ |
| Propionic Acid-Water-n-Hexane | -1.0336 | 0.9364 | 0.9865 | -1.0935 | 1.0785 | 0.9704 |
| Propionic Acid-Water-Cyclohexane | -1.4974 | 0.8632 | 0.9770 | -1.4951 | 0.9261 | 0.9746 |
| Propionic Acid-Water-Cyclohexanol | 1.8999 | 1.1764 | 0.9888 | 1.3953 | 1.0486 | 0.9932 |
| Propionic Acid-Water-Cyclohexyl | 1.6079 | 1.4186 | 0.9978 | 1.2472 | 1.2946 | 0.9981 |
| Acetate |  |  |  |  |  |  |

Brazilian Journal of Chemical Engineering Vol. 21, No. 04, pp. 647-657, October - December 2004


Figure 3: Experimental and Predicted Ternary Diagram for the Propionic Acid (1)-Water (2) - n-Hexane (3) System at 298.15 K


Solubility Curve Data
$\diamond$ Tie Line Data
--- UNIFAC
Figure 4: Experimental and Predicted Ternary Diagram for the Propionic Acid (1)-Water (2) - Cyclohexane (3) System at 298.15 K


Solubility Curve Data $\diamond$ Tie Line Data
○--- UNIFAC
Figure 5: Experimental and Predicted Ternary Diagram for the Propionic Acid (1)-Water (2) - Cyclohexanol (3) System at 298.15 K


Solubility Curve Data


Figure 6: Experimental and Predicted Ternary Diagram for the Propionic Acid
(1)-Water (2) - Cyclohexyl Acetate (3) System at 298.15 K

Table 9: Group-Volume $\left(\mathrm{R}_{\mathrm{k}}\right)$ and Surface-Area $\left(\mathrm{Q}_{\mathrm{k}}\right)$ Parameters*.

| $\mathbf{0 ,}$ | Subgroup <br> no. | Group <br> or <br> Subgroup | $\mathbf{R}_{\mathbf{k}}$ | $\mathbf{Q}_{\mathbf{k}}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | CH3 | 0.9011 | 0.848 |
| 1 | 2 | CH2 | 0.6744 | 0.540 |
| 1 | 3 | CH | 0.4469 | 0.228 |
| 5 | 15 | OH | 1.0000 | 1.200 |
| 7 | 17 | H2O | 0.9200 | 1.400 |
| 11 | 22 | CH3C | 1.9031 | 1.728 |
| 20 | 43 | OO | COOH | 1.3013 |

* Reid, R.C., Prausnitz, J.M., Poling, B.E., The Properties of Gases and Liquids, Fourth ed., McGraw-Hill Inc., ISBN 0-07-051799-1, Mexico, (1987).

Table 10: UNIFAC Group Interaction Parameters $\mathbf{a}_{\mathrm{mn}}$, in Kelvins *.

| Main <br> Group <br> no. | $\mathbf{1}$ | $\mathbf{5}$ | $\mathbf{7}$ | $\mathbf{1 1}$ | $\mathbf{2 0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | 0 | 986.5 | 1318 | 232.1 | 663.5 |
| $\mathbf{5}$ | 156.4 | 0 | 353.5 | 101.1 | 199 |
| $\mathbf{7}$ | 300 | -229.1 | 0 | 72.87 | -14.09 |
| $\mathbf{1 1}$ | 114.8 | 245.4 | 200.8 | 0 | 660.2 |
| $\mathbf{2 0}$ | 315.3 | -151 | -66.17 | -256.3 | 0 |

* Reid, R.C., Prausnitz, J.M., Poling, B.E., The Properties of Gases and Liquids, Fourth ed., McGraw-Hill Inc., ISBN 0-07-051799-1, Mexico, (1987).

Table 11: The Root Mean Square Deviation Values for the UNIFAC-Predicted and Experimental Data.

| System | RMSD |  |
| :--- | :--- | ---: |
| 1 | Propionic Acid-Water-Cyclohexanol | 2.65 |
| 2 | Propionic Acid-Water-Cyclohexyl Acetate | 5.02 |
| 3 | Propionic Acid-Water-Cyclohexane | 8.83 |
| 4 | Propionic Acid-Water-n-Hexane | 11.32 |

## CONCLUSIONS

Considering the two-phase region, it can be said that n-hexane and cyclohexane are suitable extraction agent for aqueous propionic acid mixture, on the other hand distribution coefficient values show that cyclohexanol and cyclohexyl acetate are more suitable. When the all properties are taken into consideration it can be concluded that cyclohexyl acetate is the most suitable extractant studied in this research.

The slopes of experimental and UNIFACpredicted data are similar for propionic acid-watercyclohexanol and propionic acid-water-cyclohexyl acetate systems but different for propionic acid-water-n-hexane and propionic acid-watercyclohexane systems. RMSD values show that UNIFAC gives the best fit for propionic acid-watercyclohexanol system.

Both the Othmer-Tobias and the Hand equations show a good correlation and straight lines for each ternary.

## ACKNOWLEDGEMENT

This work was supported by the Research Found of Istanbul University. Project Number: T912/06112000

## NOMENCLATURE

| $\mathrm{a}_{1}, \mathrm{~b}_{1}$ | Othmer-Tobias equation constant <br> $\mathrm{a}_{2}, \mathrm{~b}_{2}$ |
| :--- | :--- |
| Hand equation constant <br> b.p. | Boiling point $\left[{ }^{0} \mathrm{C}\right]$ |
| d | Specific gravity $[\mathrm{kg} / \mathrm{L}]$ |
| $\mathrm{D}_{\mathrm{i}}$ | Distribution coefficient of the $\mathrm{i}^{\text {ch }}$ <br> component |
| M | Molecular mass $[\mathrm{g} / \mathrm{g}-\mathrm{mol}]$ |
| $\mathrm{n}_{\mathrm{D}}$ | Refractive index |
| $\mathrm{r}^{2}$ | Othmer-Tobias and Hand correlation <br> factor |
| S | Separation factor <br> Mass fraction of the $\mathrm{i}^{\text {th }}$ component |
| $\mathrm{W}_{\mathrm{i}}$ | Mass fraction of the $\mathrm{i}^{\text {th }}$ component in <br> the aqueous phase |
| $\mathrm{W}_{\mathrm{i} 2}$ | Mass fraction of the $\mathrm{i}^{\text {th }}$ component in <br> the solvent phase |
| $\mathrm{W}_{\mathrm{i} 3}$ |  |

## REFERENCES

Alders, Liquid-liquid Extraction, $2^{\text {nd }}$ ed., Elsevier, Amsterdam (1959).
Arce, A., Blanco, A., Sauza, P. and Vidal, I., LiquidLiquid Equilibria of the Ternary Mixtures Water + Propanoic Acid + Methyl Ethyl Ketone and Water + Propanoic Acid + Methyl Propyl Ketone, J. Chem. Eng. Data, 40, 225-229 (1995).

Arce, A., Blanco, A., Sauza, P. and Vidal, I., LiquidLiquid Equilibria of the Ternary System Water + Propanoic Acid + Methyl Isobutyl Ketone at Various Temperatures, J. Chem. Eng. Data, 38, 201-203 (1993).
Badakhshan, A., Chowdhury, A.I. and Leung, R., Effect of Temperature on Liquid-Liquid Equilibria for Three Systems Containing Acetic Acid-Water-Toluene, Propionic Acid-WaterCyclohexane, Propionic Acid-Water-Toluene at Atmospheric Pressure, J. Chem. Eng. Data, 30, 416-421 (1985).
Brandani, V., Chianese, A. and Rossi, M., Ternary

Liquid-Liquid Equilibrium Data for the Water-Ethanol-Benzene System, J. Chem. Eng. Data, 30, 27 (1985).
Cehreli, S., Liquid-Liquid Equilibria of the Acetic Acid-Water-Mixed Solvent (Cyclohexyl AcetateCyclohexanol) System, Braz. J. Chem. Eng., Vol. 19, No. 01, 45-53 (2002).
Cehreli, S., Tatli, B. and Dramur, U., Liquid-Liquid Equilibria of Water-Propionic Acid-Solvent (nButyl Acetate, Propyl Acetate and Isopropyl Acetate) Ternaries, Chimica Acta Turcica, 27 (2), 53-61 (1999).
Fandary, M.S.H., Aljimaz, A.S. and Al-Kandary, J.A., Liquid-Liquid Equilibria for the System Water+Ethanol+Ethyl tert-Butyl Ether, J. Chem. Eng. Data, 44, 1129-1131 (1999).
Fredenslund, A., Jones, R.L. and Prausnitz, J.M., Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures, AIChE Journal; vol. 21, No. 6, 1086-1099 (1975).
Othmer, T.F. and Tobias, P.E., Tie Line Correlation, Ind. Eng. Chemistry, 34, No. 6, 693-696 (1942).
Radwan, G.M., Al Muhtaseb, S.A., Phase Equilibria of The Ternary System Water + Propionic Acid + 2-Butanol, Separation Science and Technology, 32 (8), 1463-1476 (1997).
Reid, R.C., Prausnitz, J.M., Poling, B.E., The Properties of Gases and Liquids, Fourth ed., McGraw-Hill Inc., ISBN 0-07-051799-1, Mexico, (1987).

Sólimo, H.N., Bonatti, C.M., Zurita, J.L. and Gramajo de Doz, M.B., Liquid-Liquid Equilibria for the System Water + Propionic Acid + 1Butanol at 303.2 K. Effect of Addition of Sodium Chloride, Fluid Phase Equilibria, 137, 163-172 (1997).

Weast, R.C. (Editor), Handbook of Chemistry and Physics, $70^{\text {th }}$ ed., CRC Press, Boca Raton, Florida (1989-1990).
Yoshizawa, H., Uemura, Y., Kawano, Y. and Hatate, Y., Equilibrium of Aqueous Propionic Acid with Trioctylamine in Dodecane, J. Chem. Eng. Data, 39, 777-780 (1994).
Zurita, J.L., Gramajo de Doz, M.B., Bonatti, C.M. and Sólimo, H.N., Effect of Addition of Calcium Chloride on the Liquid-Liquid Equilibria of the Water + Propionic Acid + 1-Butanol System at 303.15 K., J. Chem. Eng. Data, 43, 1039-1042 (1998).

